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The heating rate influence on the elastic modulus temperature dependence of a corrosion-resistant nickel alloy

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Abstract. The temperature dependence of the elastic modulus of nickel-chromium-molybdenum alloy C4 was investigated by the method of dynamic mechanical analysis. At all heating rates, an abnormal increase in the elastic modulus is observed upon heating in the temperature range of 200-300 °C. It is shown that an increase in the heating rate shifts the beginning of the observed effect to the region of higher temperatures. The temperature anomaly in the elastic modulus of the C4 alloy is explained from the standpoint of the formation of a short-range order in a solid solution. The thermodynamically equilibrium temperature of the “disorder – short-range order” transition in C4 alloy is determined to be 205 °C.

1. Introduction

Nickel-chromium-molybdenum alloys are one of the main structural materials of the chemical industry and nuclear energy. Their use is caused by high corrosion resistance both at room and at elevated (up to 400 °C) temperatures [1, 2]. It is also proposed to use these alloys in the environment of molten chlorides at elevated temperatures (350-650 °C) [3].

It is known that in the indicated temperature range, short-range and long-range effects are observed in alloys of the Ni-Cr-Mo system. The appearance and destruction of ordered structures is accompanied by a change in the forces of interatomic interaction in the alloy, which affects the physical properties of the alloy and its corrosion resistance. Properties such as specific heat, thermal diffusivity, Coefficient of Thermal Expansion (CTE), and electrical resistivity are fairly well studied for nickel-chromium and nickel-chromium-molybdenum alloys of different chemical compositions. The nonlinear nature of the change in these properties with temperature is general. Basically, the excesses on the curves “temperature - property” are associated with the transitions “disorder - short-range order - long-range order - short-range order” [4–8]. However, literature data on changes in the elastic modulus of these alloys upon heating and cooling are rather scarce.

Thus, the nonlinear nature of the Young's modulus of pure nickel during heating and cooling was shown in [9] (Fig. 1). Below the Curie temperature, the measurements were carried out in a saturating magnetic field. The effect was attributed to the influence of residual stresses on magnetic ordering.

In [10], the authors investigated the bulk modulus of elasticity of Ni–Cr, Fe–Ni–Cr–Mo, and Mn–Fe alloys. In the latter case, an anomaly was observed in the curve at a temperature of 470 K. The researchers associated this effect (Fig. 2) in an alloy of the Mn-Fe system with antiferromagnetic ordering. Unfortunately, there was no explanation why in the Ni-Cr system (also a ferromagnet-antiferromagnet pair) such an anomaly was not found. In the educational literature [11] it is indicated that the formation of short-range order (known as the K-state) in this system leads to an increase in the elastic modulus by 1.5%. The existence of different explanations for the same effect requires additional study of this issue.

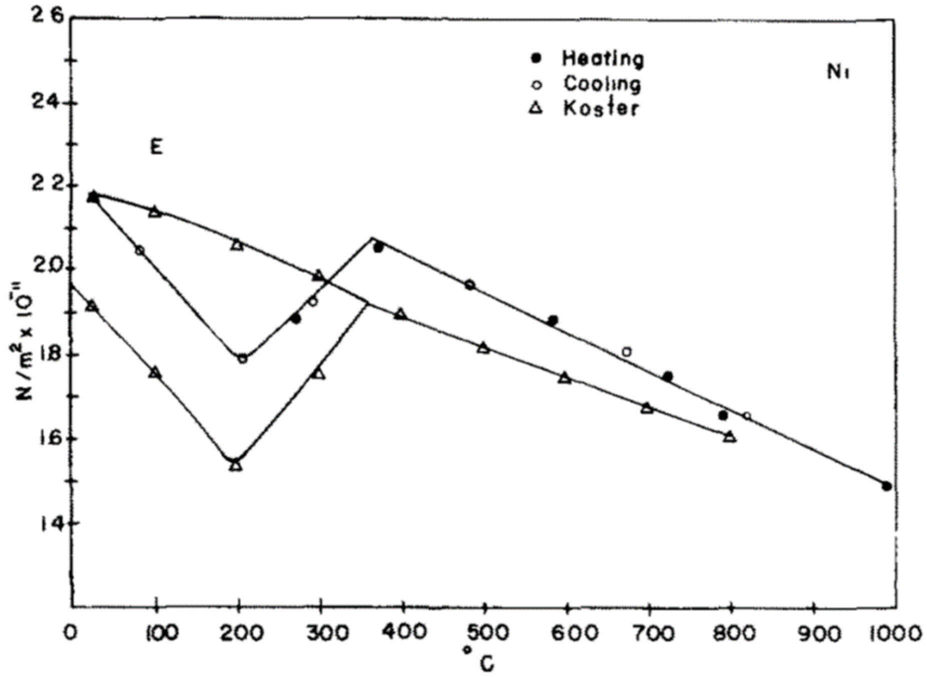

Figure 1. The temperature dependence of Young's modulus of nickel [9]

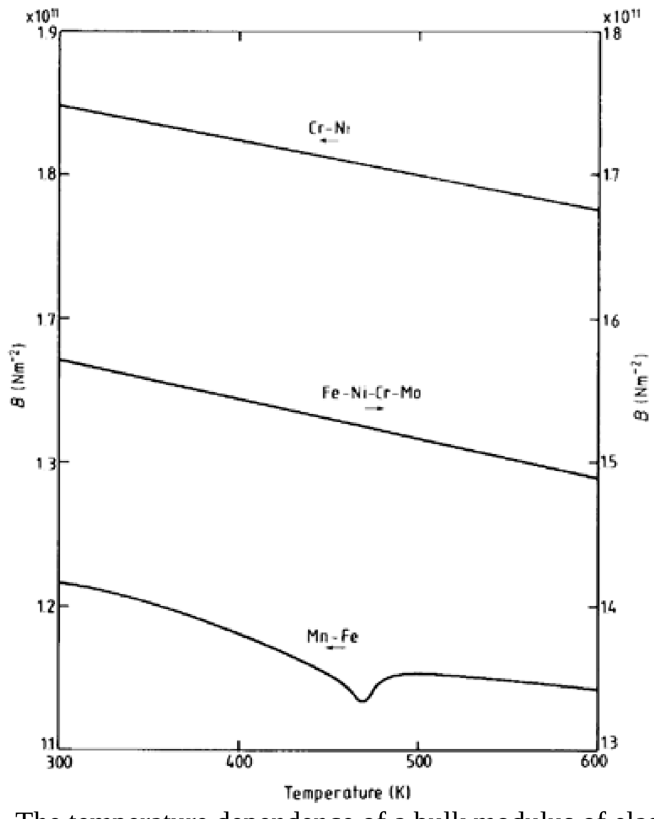

Figure 2. The temperature dependence of a bulk modulus of elasticity [10]

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The aim of this work is to investigate and analyze the influence of the heating rate on the temperature dependence of the elastic modulus of a corrosion-resistant alloy of the Ni-Cr-Mo system.

2. Materials and methods

The research material was nickel-chromium-molybdenum alloy C4. The chemical composition, wt. %: Cr 14.5 ... 17.5%; Mo 14.0 ... 17.0%; Fe not more than 3.0%; P no more than 0,020%; Ti not more than 0.7%; Co not more than 2.0%; Si not more than 0.05%; S not more than 0.010%; C not more than 0.009%; Mn not more than 1.0%.

The determination of the elastic modulus of the alloy was carried out by the dynamic mechanical analysis method using Netzsch DMA 242 C instrument, and the samples were deformed according to a three-point bending scheme. In the experiment, a plate with a width of 4 ± 0.2 mm and a thickness of 1.5 ± 0.2 mm was loaded with a cyclic load of 5.3 N at a frequency of 1 Hz, leading to elastic deformation, and the temperature was raised to 500 ° C. During heating, the change in the elastic modulus of the sample was recorded and the dependence of the elastic modulus on the temperature function was obtained.

Metallographic analysis was performed using a Jeol JSM-6490LV scanning electron microscope in the backscattered electron mode (orientation-compositional contrast).

X-ray diffraction analysis (XRD) was carried out on a Bruker D8 Advance X-ray diffractometer using Kα Cu radiation (filtering using a Sol-X energy dispersive detector) in the range of reflection angles 2°=30-140° at voltage U = 40 kV, current tubes I = 40 mA using the incident beam Soller slots; the measuring diameter was 500 mm, the step was 0.02°, the pulse set time at each step was from 3 to 5 s. Qualitative phase analysis was performed in the DiffracPlus® EVA software package by selecting standards from the ICDD PDF2 database of X-ray diffraction spectra.

In the manufacture of thin sections, alloy samples were processed on sandpaper with a sequential decrease in the abrasive fraction of the paper to the minimum using the Struers LaboPol-5 installation, and then polished on diamond suspensions with a decrease in the fraction from 9 to 1 μm. To obtain orientation-compositional contrast in a SEM, it is necessary to remove the surface stresses that arose during mechanical processing, so the samples were subjected to final polishing on colloidal silicon.

3. Results and discussion

According to the data of X-ray phase analysis, the main phase in the C4 alloy is γ - a solid solution based on nickel (Figure 3). The metallographic images obtained by SEM show the grain structure of the C4 alloy (Figure 4). The grain size ranges from 100-200 microns. Inside the grains there are a large number of annealing twins, which is typical for nickel-chromium-molybdenum alloys in the quenched state.

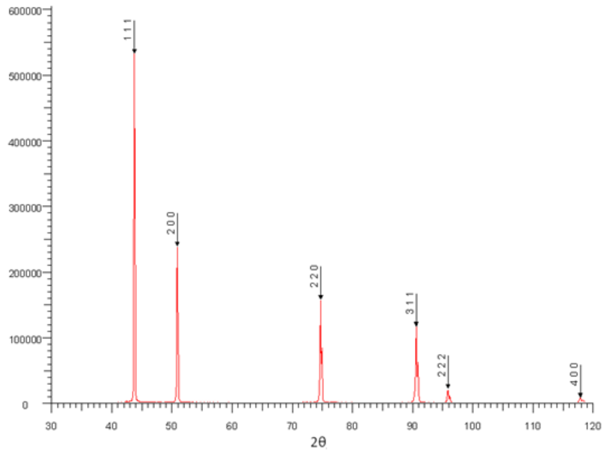

Figure 3. XRD of C4 alloy

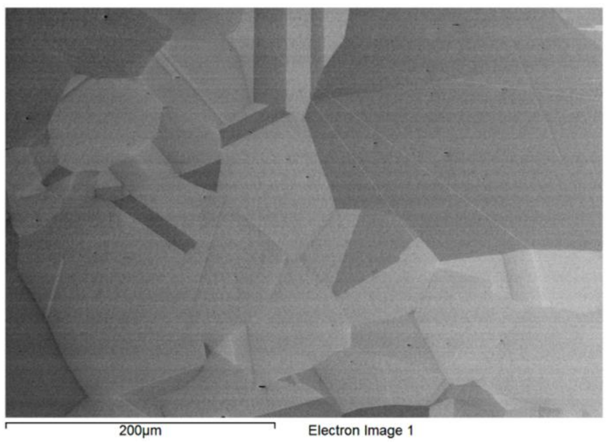

Figure 4. The structure of C4 alloy

Figures 3.4 and 3.5 show the results of an X-ray diffraction phase analysis during heating in a heat chamber. The kink at the temperature of 550 °C on line 222 (second) of the solid solution is clearly visible on the heating curve (Figure 5a). Such a kink indicates an increase in the growth rate of the sample volume above temperatures of 550 °C. This behavior can be explained by a decrease in the interatomic interaction forces caused by short-range order destruction, which, according to the literature, exists in Ni-Cr-Mo alloys in the temperature range from room temperature to 600 °C. During cooling, such inflection is also observed, but less pronounced, which indicates the restoration of short-range order in the temperature range of 550 °C (Figure 5b). No effects are observed on the thermal diffractogram from room temperature to 550 °C.

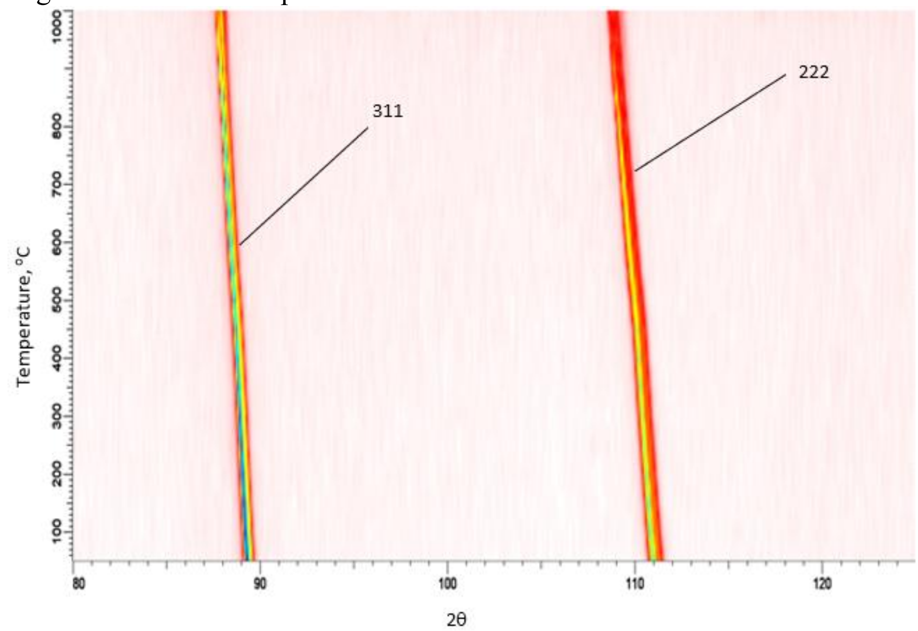

Figure 5a. Thermo-XRD of C4 alloy (heating)

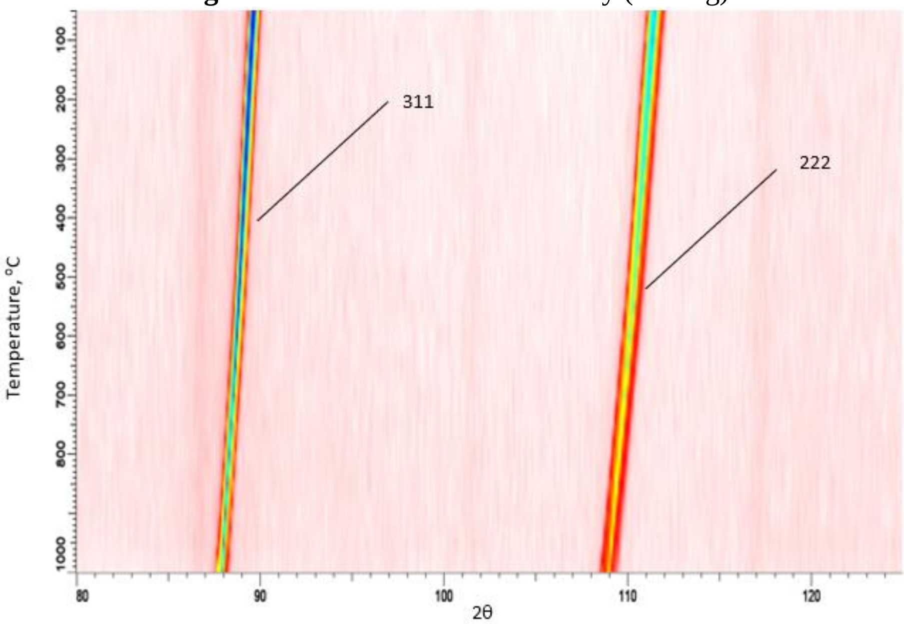

Figure 5b. Thermo-XRD of C4 alloy (cooling)

In this work, four measurements of the elastic modulus were carried out at different heating rates of the sample by dynamic mechanical analysis. The values obtained at room temperature fluctuate in the range of 210-215 GPa, which is in good agreement with the known data for this alloy. The relative change in the elastic modulus during heating for different heating rates is shown in Fig. 6.

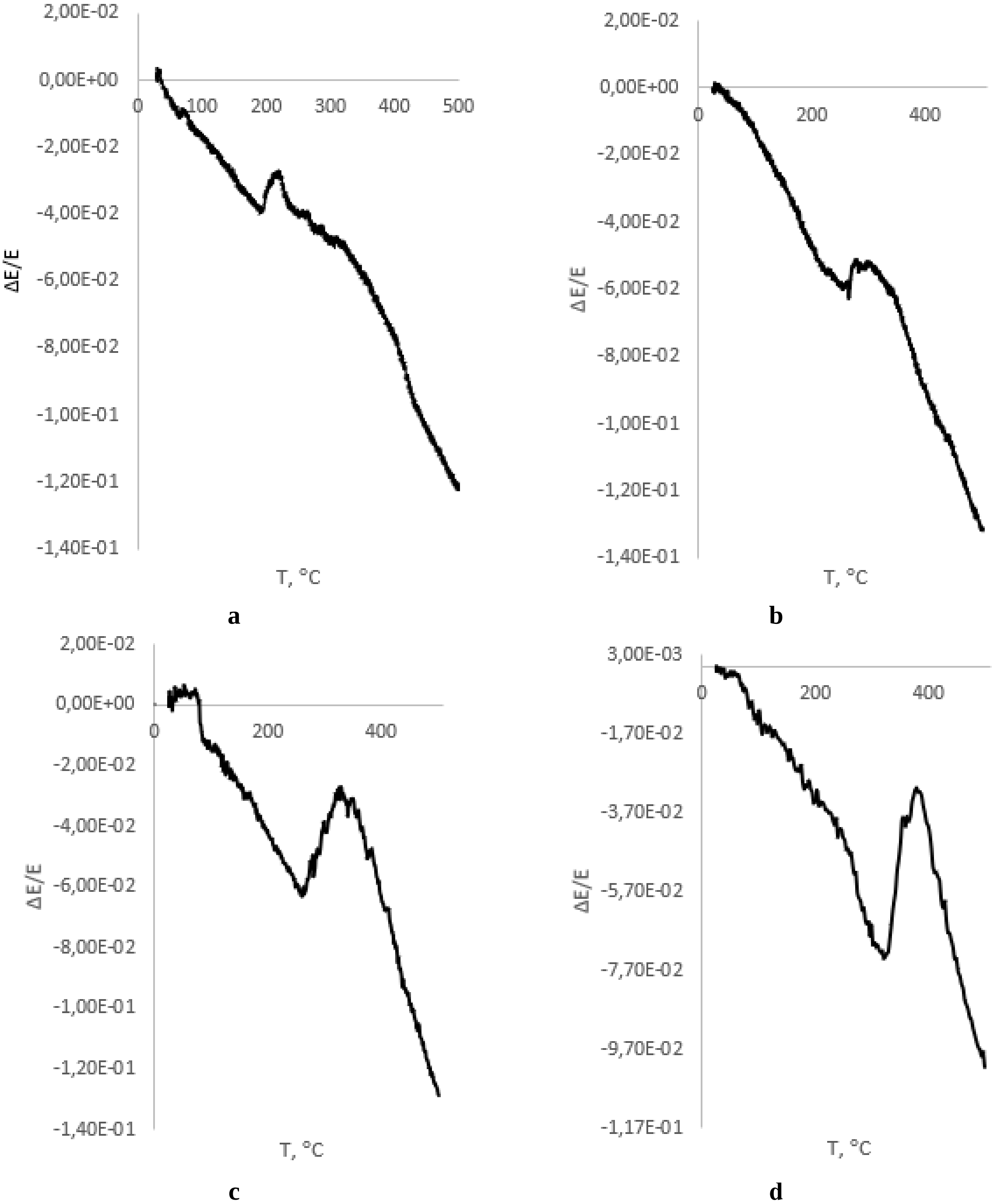

Figure 6. The dependence of elastic modulus as a function of temperature for C4 alloy
a- heating rate 1 °C/min; b- heating rate 5 °C/min; c- heating rate 10 °C/min; d- heating rate 20 °C/min

The inflection temperatures for all heating rates were determined graphically. They were determined to be 193 °C, 260 °C, 263 °C, 324 °C for heating rates of 1 °C/min, 5 °C/min, 10 °C/min, 20 °C/min, respectively. The shift of the inflection point to the region of higher temperatures with increasing heating rate is apparently associated with the leading role of diffusion in the process of formation of short-range order. Based on the obtained data, a dependence graph of the inflection temperature on the heating rate was constructed (Figure 7). The approximation shows a linear relationship with a correlation coefficient of R^2=0.8687. Extrapolation of this line to a zero heating rate gives an equilibrium inflection temperature, i.e. transition temperature "disorder - short range order". In our case, this temperature is 205 °C.

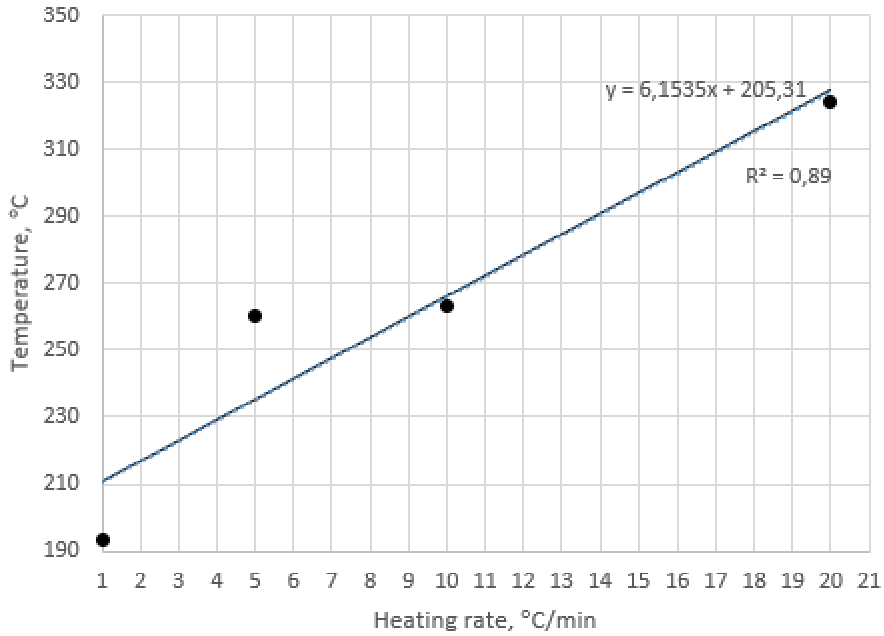

Figure 7. A dependence graph of the inflection temperature on the heating rate

The true causes of the anomaly in the elastic modulus have not been established by the methods used in this work. However, the fact that the temperature at which the anomaly occurs depends on the heating rate indicates the non-magnetic nature of this effect. The driving force of the process is diffusion, and the explanation of it by the formation of short-range order in our opinion is more correct. In addition, it is interesting that there is no reverse disorder – short-range transition during cooling (Figure 8). Herewith, the increase in the elastic modulus is about 15% relative to the initial value.

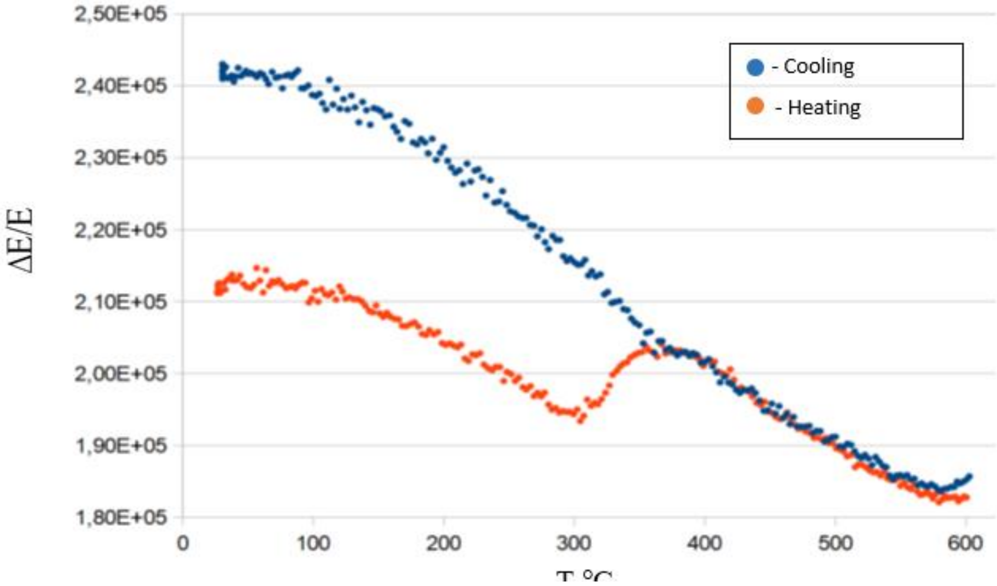

Figure 8. The dependence of elastic modulus as a function of temperature for C4 alloy

4. Conclusion

Using dynamic mechanical analysis, the dependence of the elastic modulus anomaly temperature of the C4 alloy on the heating rate was established. This indicates diffusion as the driving force of the process causing this effect. Comparing the obtained results with the published data, the cause of the temperature anomaly in the nickel-chromium-molybdenum alloy is the “disorder – short-range order” transition.

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